

# PATENT SPECIFICATION

(11) 1 454 852

1 454 852

- (21) Application No. 30926/74 (22) Filed 12 July 1974  
 (31) Convention Application No. 2 335 687  
 (32) Filed 13 July 1973 in  
 (33) Germany (DT)  
 (44) Complete Specification published 3 Nov. 1976  
 (51) INT CL<sup>2</sup> C07C 39/12, 39/16  
 (52) Index at acceptance  
 C2C 220 227 22Y 292 29Y 30Y 313 31Y 338 365 36Y 633  
 662 699 WM  
 (72) Inventors HUGO VERNALEKEN, LUDWIG BOTTENBRUCH,  
 GERHARD EMMER and UWE HUCKS



## (54) A METHOD OF AND AN INSTALLATION FOR THE CONTINUOUS PRODUCTION OF AQUEOUS DIALKALI SALT SOLUTIONS OF AROMATIC DIHYDROXY COMPOUNDS

(71) We, BAYER AKTIENGESSELLSCHAFT, Leverkusen, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for continuously producing solutions of dialkali or dialkaline earth metal salts of aromatic dihydroxy compounds.

Aqueous dialkali salt solutions of aromatic dihydroxy compounds are generally produced in batches by introducing a weighed quantity of the corresponding dihydroxy compound, preferably freed from traces of oxygen beforehand by degassing or rinsing with nitrogen, into a dilute aqueous alkali hydroxide solution. This process is normally carried out in stirrer-equipped vessels. The residence time is governed by the size of the batch and generally amounts to between 60 and 180 minutes for batches of from 0.5 to 2 tonne of dihydroxy compound.

It is possible in this way to produce dialkali salt solutions with a reproducible, narrow tolerance range in regard to solids concentration. Difficulties are involved in removing the traces of oxygen. Oxygen is undesirable in solutions of this kind, because it results in discolouration thereof. Discolouration attributable to the influence of oxygen is often the cause of defective colouring in polycarbonates produced from solutions of this kind.

The batch production of dialkali salt solutions is unsuitable for the production of polycarbonates on a fairly large scale. Dialkali salts can only be continuously prepared in a cascade of stirrer-equipped vessels at considerable expense. Particular difficulties are involved in continuously introducing the starting products and in degassing the solid.

The object of the invention is to provide a simple, reliable method for the continuous pro-

duction of solutions of dialkali or dialkaline earth metal salts of aromatic dihydroxy compounds. According to the invention, there is provided a process for continuously producing solutions of dialkali or dialkaline earth metal salts of aromatic dihydroxy compounds, wherein an aromatic dihydroxy compound is sprayed in the form of a melt onto a turbulent liquid film of a solution of an alkali or alkaline earth metal hydroxide.

The particular advantage of the method according to the invention is that the reaction times required for dissolving the aromatic dihydroxy compounds are extremely short, amounting to less than 1 minute. Since all the component streams are introduced as liquids in the method according to the invention, dialkali salt solutions with solids and alkali concentrations in a predetermined, narrow tolerance range are obtained. An unexpected advantage of the method according to the invention is the very good colour quality of the dialkali salt solutions and of the polycarbonates obtainable from them. The very good colour quality is surprising because aromatic dihydroxy compounds show a tendency to undergo cleavage reactions at elevated temperatures, especially in the presence of alkali.

In one embodiment of the method according to the invention, the liquid film is produced in a reactor by tangentially introducing a component stream of the aqueous alkali hydroxide solution, and spraying the molten dihydroxy compounds through nozzles.

The particular advantage of this embodiment of the method according to the invention is that it produces a uniform liquid film of the aqueous alkali hydroxide solution onto which the molten dihydroxy compound is sprayed in the form of fine particles.

In another embodiment of the method according to the invention, the melts of the dihydroxy compounds are sprayed through a nozzle system into a cylindrical reactor onto,

50

55

60

65

70

75

80

85

90

and dissolved in, the turbulent liquid film in a defined quantity, the reactor being provided with cooling systems and the turbulent liquid film being produced by tangentially introducing a defined stream of an aqueous alkali hydroxide solution and a component stream of the reaction solution which can amount to between 0.5 and 20 times the aqueous alkali hydroxide solution introduced.

The particular advantage of this embodiment of the method according to the invention is that conversion can be controlled during the reaction, in addition to which undesirable temperatures ranges are avoided.

In order to minimise thermal stressing of the reaction product, the installation is designed in such a way that, in another embodiment of the method according to the invention, the average residence time of the aqueous dialkali salt solutions of the aromatic dihydroxy compounds amounts to between about 0.5 to 20 minutes.

In another embodiment of the method according to the invention, virtually any aromatic dihydroxy compounds and mixtures thereof which, in the form of melts, are stable for at least one minute and whose alkali salts have the necessary solubility in water, can be used for the reaction. The method is preferably used for the production of dialkali salt solutions of dihydroxy diarylalkanes, such as for example, 4,4' - dihydroxy - 2,2 - diphenylpropane; 4,4' - dihydroxy - 1,1 - diphenylcyclohexane; 4,4' - dihydroxy - 3,3',5,5' - tetramethyl - 2,2 - diphenylpropane; 4,4' - dihydroxy - 3,3',5,5' - tetrachloro - 2,2 - diphenylpropane; 4,4' - dihydroxy - 3,3',5,5' - tetrabromo - 2,2 - diphenylpropane. Sodium hydroxide is preferably used as the aqueous alkali hydroxide solution.

In the accompanying drawing: Figure 1 is a diagrammatic illustration of an apparatus for use in carrying out the process according to the present invention. Figure 2 is a section on line A—B in Figure 1.

The principle outlined above is described in more detail in the following with reference to one preferred embodiment of the method according to the invention. In this embodiment of the method according to the invention, which is illustrated in Figure 1, an aromatic dihydroxy compound is melted in an appropriate vessel 1 and delivered by a pump 2, acting as a metering unit, through a heated pipe 3 into a reactor 4. The aqueous alkali solution, which may optionally contain special additives, is pumped through a pipe 6 into the reactor 4 by a delivery pump unit 5. The throughflows of the product streams introduced are controlled and recorded by means of throughflow meters 7 and 8.

The reactor 4 comprises a cylindrical container 9 and two covers 10 and 11. The cover 11 is heatable. A tubular coil 12, through

which the heat of solution and reaction is dissipated, is installed in the lower part of the cylindrical container 9.

As shown in Figure 2 (which is a section on the line A—B of Figure 1), the upper part of the reactor comprises at least two, but advantageously several, tangential inlets 13 through which the reaction solution is introduced, so that a liquid film 14 is formed.

The melt of the aromatic dihydroxy compound is introduced from the vessel 1 through a heated pipe 15 into a similarly heated distributor chamber 16 and is sprayed through the nozzles 17, arranged around the periphery of the distributor chamber 16, onto the liquid film 14 where the dialkali salt solution is spontaneously formed.

The required development of the liquid film 14 is obtained by running in the aqueous alkali hydroxide solution through the pipe 6, and by introducing a component stream of the reaction solution from the reactor 4, which generally amounts to between 0.5 and 20 times the product stream from the pipe 6, through a pump 18 and a pipe 19. A ring pipe 20 distributes the stream of liquid from the pipe 19 to individual insertion tubes 21 which are introduced into the reactor through the inlets 13. The cross-sections of the insertion tubes 21 are of such dimensions that the liquid issuing from them produces the liquid film 14.

The dialkali salt solutions is removed from the stream of liquid delivered by the pump 18 by means of regulators 22 and 23 and a flow meter 25 into a pipe 24 for further use.

By virtue of the method described above, it is possible, despite short reaction times, to produce from the melts of aromatic dihydroxy compounds the corresponding aqueous dialkali salt solutions both continuously and with a reproducible solids concentration. Instead of using an alkali hydroxide solution, it is also possible to use an alkaline earth hydroxide solution. In addition, it is possible to use this process for the production of solutions of dihydroxy compounds in organic solvents.

#### Example.

By introducing a bisphenol melt and a solution of sodium hydroxide in water, disodium bisphenolate solutions 1 to 7 are continuously produced in an apparatus as described with reference to the accompanying drawings which has a volume of 16 litres and a pump recirculation capacity of 900 litres per hour. The test parameters are shown in the following Table. For comparison, corresponding disodium bisphenolate solutions are prepared in batches in an 800 litre capacity vessel. The following procedure is applied for this purpose: a dilute sodium hydroxide is prepared by introducing water and 45% by weight sodium hydroxide into a stirrer-equipped

vessel. The dihydroxy compounds 1, 5, 6, 7 are introduced as solids, in the form of flakes, with vigorous stirring into these solutions over a period of 20 minutes in two portions. The required bisphenolate solutions are obtained

after a total reaction time of 90 to 130 minutes. The colour values of these batches and the necessary dissolution times are shown in the Table. For comparison, the volume-time yields of both processes are also quoted.

5

Dihydroxy compound	Temp. [°C]	Through-put [kg/h]	Residence time [mins.]	Sodium hydroxide		VTY [kg/l.h]	r*)	Bis-phenolate solution % solids	CV [Hz]	Non-continuous batch for comparison		
				conc. [% by weight]	through-put [Kg/h]					CV [Hz]	RT [min]	VTY [kg/h.l]
1. Bisphenol A	165	50	1.9	3.90	450	3.13	1	10.0	5	15	90	0.067
2.		40	3.6	6.19	226.7	2.50	2	15.0	0-5			
3.		25	5.0	8.69	**166.7	1.56	2	15.0	5			
4.		30	6.4	8.77	120	1.87	8	20.0	5	25	100	0.12
5. Tetramethyl bisphenol A	175	25	7.7	7.04	100	1.56	2	20.0	10	35	130	0.092
6. Tetrachlor bisphenol A	140	40	2.4	2.43	360	2.5	2	10.0	5-10	40	90	0.067
7. Bisphenol Z	195	40	2.4	3.32	360	2.5	2	10.0	5-10	45	120	0.05

\*) r = ratio of pump-recirculated quantity (l) to quantity introduced (l).

\*\*) use of potassium hydroxide instead of sodium hydroxide.

CV = colour value

RT = reaction time

VTY = volume-time yield

An installation for producing a liquid film with a component stream of the reaction solution for carrying out the method according to the invention is distinguished by the fact that at least two insertion tubes 21 are connected to a ring pipe 20, leading into the reactor 4 through inlets 13 and forming an angle of less than 45° with the inner wall of the reactor.

The particular advantage of the installation according to the invention is that a uniform liquid film can be produced.

#### WHAT WE CLAIM IS:—

1. A process for continuously producing solutions of dialkali or dialkaline earth metal salts of aromatic dihydroxy compounds, wherein an aromatic dihydroxy compound is sprayed in the form of a melt onto a turbulent liquid film of a solution of an alkali or alkaline earth metal hydroxide.

2. A process as claimed in claim 1, wherein the solution of an alkali or an alkaline earth metal hydroxide is an aqueous solution.

3. A process as claimed in Claim 1 or 2, wherein the liquid film is produced in a reactor by tangentially introducing a stream of the solution of an alkali or alkaline earth metal hydroxide and the molten dihydroxy compound is sprayed through nozzles.

4. A process as claimed in any preceding Claim, wherein the melt of the dihydroxy compound is sprayed through a nozzle system into a cylindrical reactor onto a turbulent

liquid film in a product stream, the reactor being provided with a cooling system and the turbulent liquid film being produced by tangentially introducing a stream of the solution of an aqueous alkali metal or alkaline earth metal hydroxide and a stream of the reaction solution which can amount to between 0.5 and 20 times the aqueous alkali hydroxide solution introduced.

5. A process as claimed in any preceding Claim, wherein the average residence time of the salt solutions of the aromatic dihydroxy compounds in the reactor is between 0.5 and 20 minutes.

6. A process as claimed in any preceding Claim, wherein the dihydroxy compounds is bisphenol A, 1,1 - bis - (4 - hydroxyphenyl) - cyclohexane, tetramethyl bisphenol A, tetrachloro bisphenol A or tetrabromo bisphenol A and the solution of an alkali or an alkaline earth metal hydroxide is a dilute aqueous solution of sodium hydroxide.

7. An apparatus when used for carrying out the process claimed in any preceding Claim, comprising at least two insertion tubes connected to a ring pipe, leading into a reactor through inlets and forming an angle of less than 45° with the wall of the reactor.

ELKINGTON & FIFE,  
Chartered Patent Agents,  
52—54 High Holborn House,  
London WC1V 6SH.  
Agents for the Applicants.

